5. Collection and Analysis of Rate Data

- **Objectives**
  - **Determine the reaction order and specific reaction rate from experimental data obtained from either batch or flow reactors**
  - **Describe how to analyze experimental data to determine the rate law**
  - **Use regression software to evaluate the rate law parameters given experimental data**
  - **Compare two or more types of laboratory reactors used to obtain rate law data along with their advantages and disadvantages**

0. Finding the Rate Law I

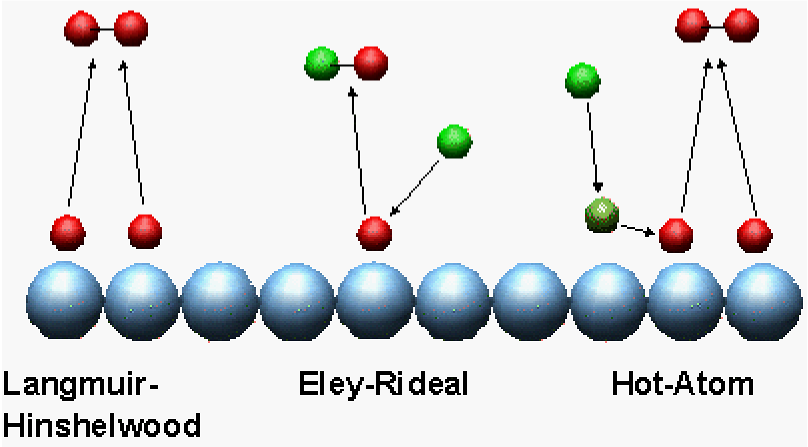
- The algorithm for data analysis 1
  - Postulate a rate law
    - power law models for homogeneous rxns

$$-r_A = kC_A^{\alpha} \qquad\qquad -r_A = kC_A^{\alpha}C_B^{\beta}$$

- Langmuir-Hinshelwood model for heterogeneous rxns

$$-r_A^{'} = \frac{kP_A}{1+kP_A},$$

$$-r_A^{'} = \frac{kP_AP_A}{(1+kP_AP_A+P_B)^2}$$



0. Finding the Rate Law II

○ The algorithm for data analysis 2

- Select reactor type and mole balance
  - batch reactor on reactant A

$$-r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt}$$

  - differential PBR

$$-r_{\mathrm{A}}^{'} = \frac{F_{\mathrm{P}}}{\Delta W} = C_{\mathrm{p}} v_0 / \Delta W$$

- Process your data in terms of measured variables
  - N_A, C_A, or P_A
- Look for simplifications
  - one reactants in excess
  - mole fraction A small $\Rightarrow \varepsilon \approx 0$

0. Finding the Rate Law III

○ **The algorithm for data analysis 3**

- Constant volume batch reactor

A → Products

- **Mole Balance:** $\frac{dN_A}{dt} = r_A V$
- **Rate Law:** $-r_A = kC_A^{\alpha}$
- **Stoichiometry:** $V = V_0$
- **Combine:** $\boxed{-\frac{dC_A}{dt} = kC_A^{\alpha}}$

1. Integral Method
2. Differential Method
3. Non-Linear Least-Squares Analysis

0. Finding the Rate Law III

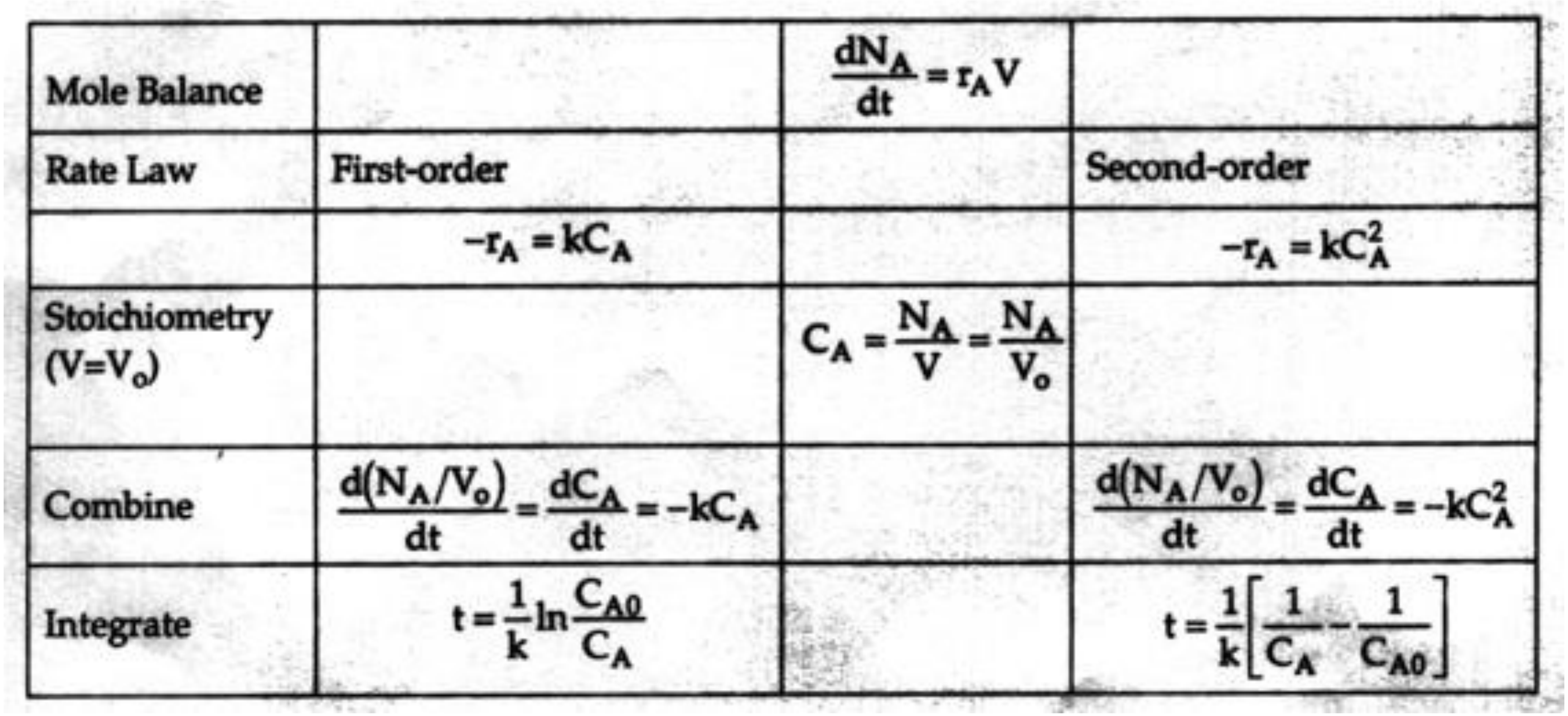
- The algorithm for data analysis 4

  - Differential PBR

    - calculate $$-r_A' = \frac{C_p v_0}{\Delta W}$$
    - choose model, e.g., $$-r_A' = \frac{kP_A}{1+kP_A},$$
    - use nonlinear regression to find the best model parameters

1. Integral Method I

- **Derivation Equations used to Plot 0, 1st, and 2nd order reactions**



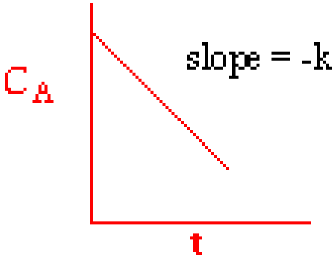
Mole Balance		$\frac{dN_A}{dt} = r_A V$	
Rate Law	First-order		Second-order
	$-r_A = kC_A$		$-r_A = kC_A^2$
Stoichiometry (V=V$_o$)		$C_A = \frac{N_A}{V} = \frac{N_A}{V_o}$	
Combine	$\frac{d(N_A/V_o)}{dt} = \frac{dC_A}{dt} = -kC_A$		$\frac{d(N_A/V_o)}{dt} = \frac{dC_A}{dt} = -kC_A^2$
Integrate	$t = \frac{1}{k}\ln\frac{C_{A0}}{C_A}$		$t = \frac{1}{k}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$

1. Integral Method II

- **To determine the values k for runs at various temp. and then used to determine the activation energy**

Zero Order

Zero order, $\alpha = 0$



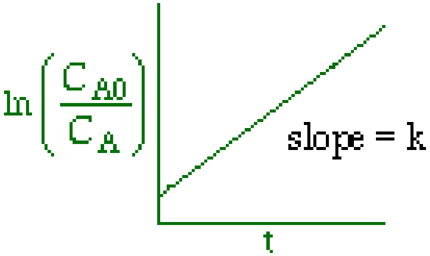
$$\frac{dC_A}{dt} = r_A = -k$$

$$\text{at } t = 0,\ C_A = C_{A0}$$

$$\Rightarrow C_A = C_{A0} - kt$$

First Order

First order $\alpha = 1$



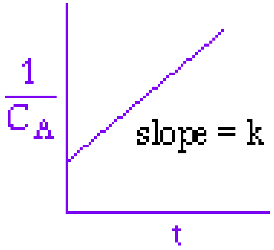
$$\frac{dC_A}{dt} = r_A = -kC_A$$

$$\text{at } t = 0,\ C_A = C_{A0}$$

$$\Rightarrow \ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

Second Order

Second order $\alpha = 2$



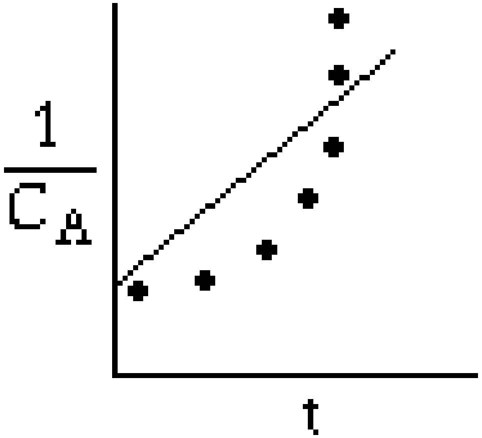
$$\frac{dC_A}{dt} = r_A = -kC_A^2$$

$$\text{at } t = 0,\ C_A = C_{A0}$$

$$\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

1. Integral Method III

- If the data do not fall on a straight line for α = 0,1, or 2 such as α = 2;



- Then we should stop guessing reaction orders and proceed to either the differential method of analysis or to regression

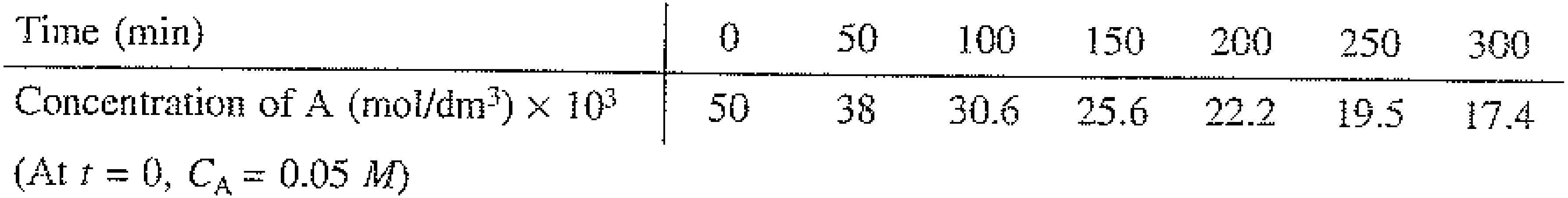
1. Integral Method IV

- **Ex 5-2, p 269 Determining the rate law 1**

  Trytil (A) + Methanol (B) → Products

  - Reaction carried out at benzene and pyridine solution at 25°C (at t = 0, C_A = 0.05 M , C_B = 0.5 M)

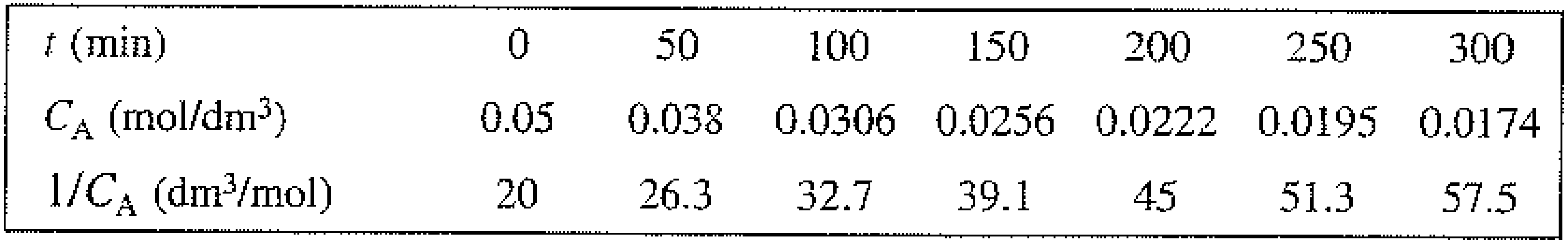
  - One product Cl reacts with pyridine and precipitates



Time (min)	0	50	100	150	200	250	300
Concentration of A (mol/dm^3) × 10^3	50	38	30.6	25.6	22.2	19.5	17.4

(At $t = 0$, $C_A = 0.05$ M)

TABLE E5-2.1. PROCESSED DATA



t (min)	0	50	100	150	200	250	300
C_A (mol/dm^3)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174
$1/C_A$ (dm^3/mol)	20	26.3	32.7	39.1	45	51.3	57.5

1. Integral Method V

- ○ **Ex 5-2, p 269 Determining the rate law 2**

- Rate law

$$-\frac{dC_A}{dt} = k^{'} C_A^{\alpha}$$

- Assume 2nd order rxn

$$-\frac{dC_A}{dt} = k^{'} C_A^{2}$$

- Integrating

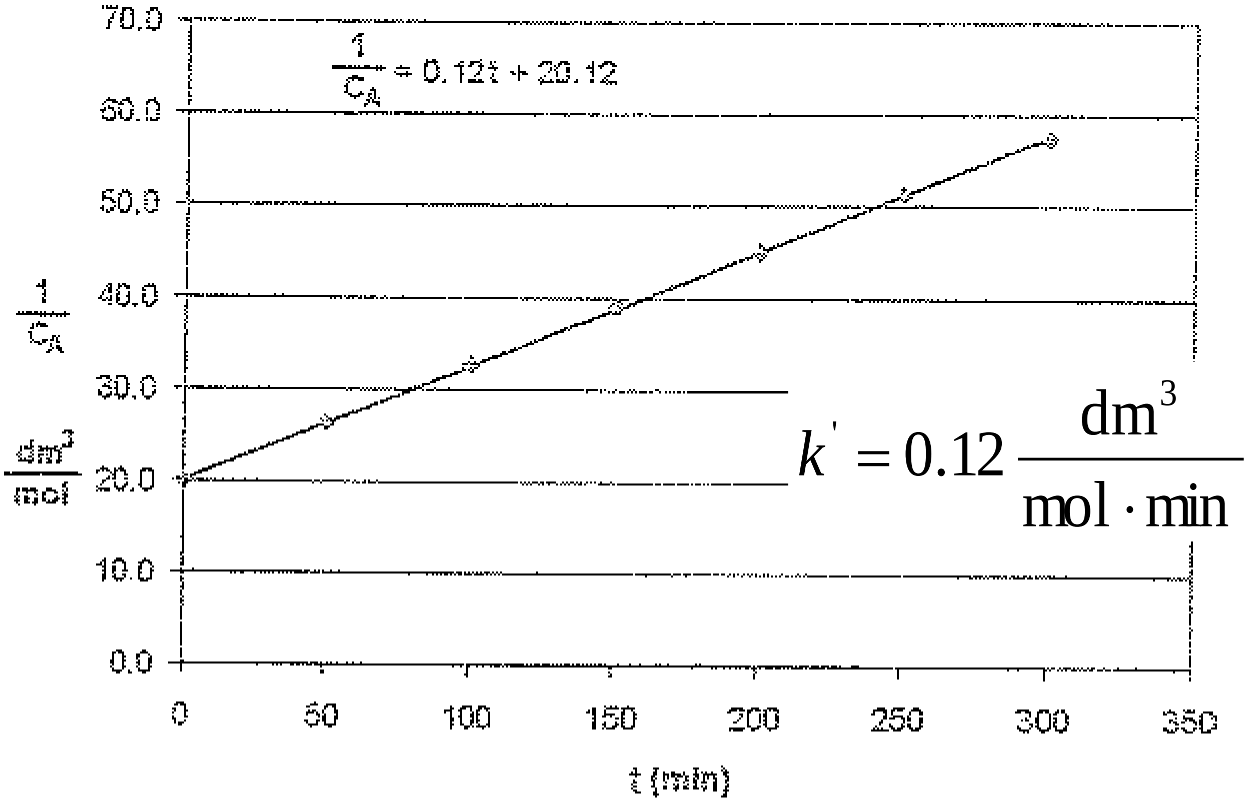
$$t = \frac{1}{k^{'}}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

- Rearranging

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k^{'} t$$

1. Integral Method VI

- **Ex 5-2, p 269 Determining the rate law 3**



$$k' = 0.12\ \frac{\mathrm{dm}^3}{\mathrm{mol} \cdot \mathrm{min}}$$

1. Integral Method VII

- **Ex 5-2, p 269 Determining the rate law 4**

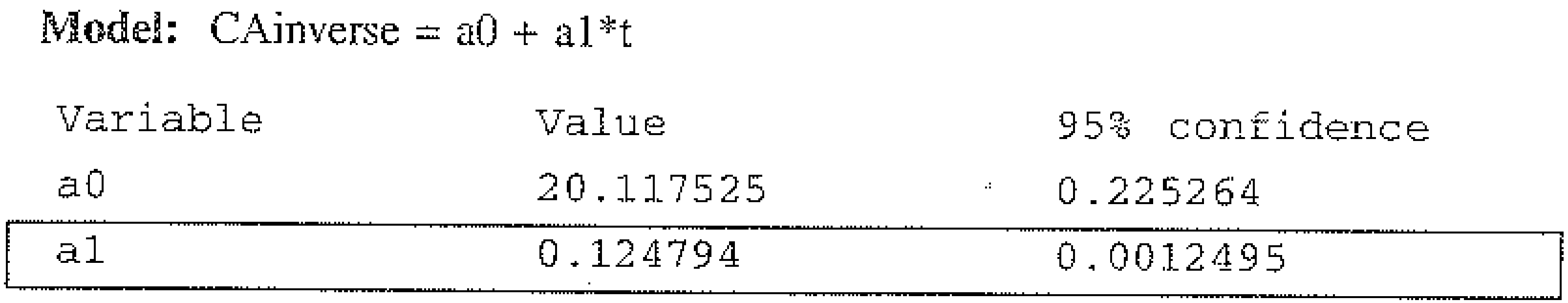
- Calculating k

$$k = \frac{k'}{C_{B0}} = \frac{0.12}{0.5} \frac{\mathrm{dm}^3/\mathrm{mol}\cdot\mathrm{min}}{\mathrm{mol}/\mathrm{dm}^3} = 0.24\left(\frac{\mathrm{dm}^3}{\mathrm{mol}}\right)^2 \Big/ \mathrm{min}$$

- Rate law

$$-r_A = \left[0.24\left(\frac{\mathrm{dm}^3}{\mathrm{mol}}\right)^2 \Big/ \mathrm{min}\right] C_A^2 C_B$$

- Polymath



```
Model:  CAinverse = a0 + a1*t

Variable             Value              95% confidence
a0                   20.117525          0.225264
a1                   0.124794           0.0012495
```

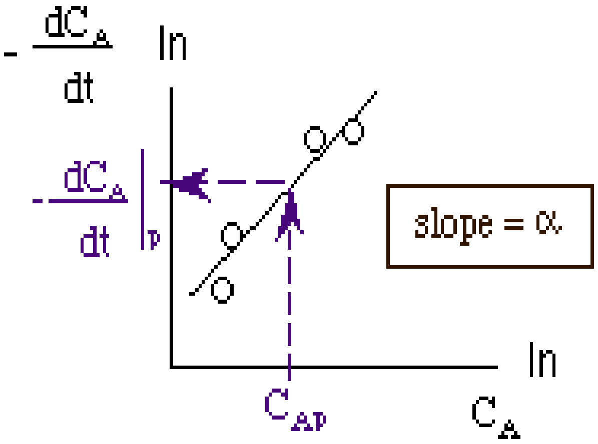
2. Differential Method p. 224

- **Taking the natural log of** $-\dfrac{dC_A}{dt} = kC_A^{\alpha}$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

- The reaction order can be found from a ln-ln plot of

$$\left(-\frac{dC_A}{dt}\right) \; vs. \; C_A$$



$$\boxed{k = \frac{-\left.\dfrac{dC_A}{dt}\right|_P}{C_{AP}^{\alpha}}}$$

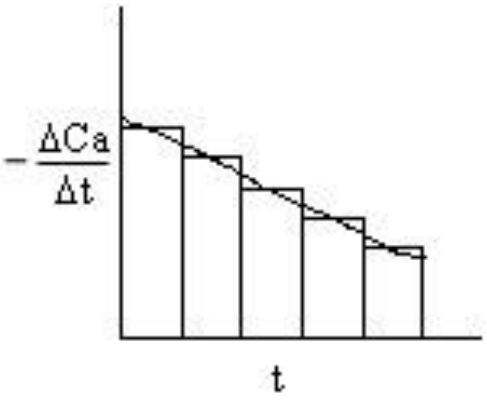
2. Differential Method II

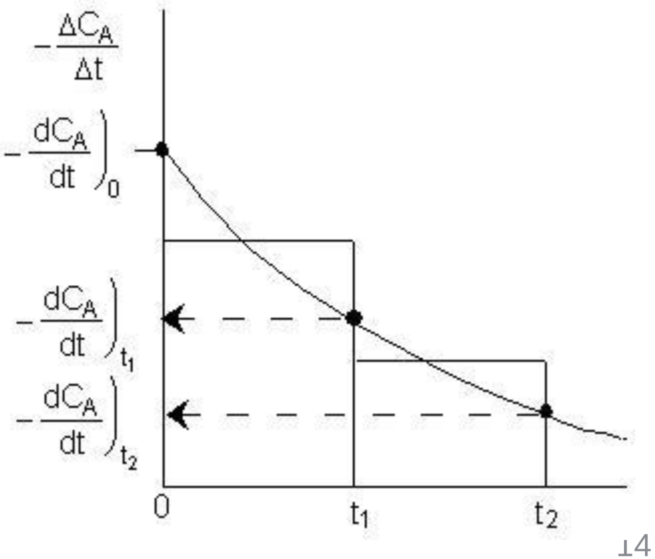
- **Given concentration as a function of time from batch reactor experiments**

time (s)	0	t_1	t_2	t_3
concentration (mol/dm^3)	C_{Ao}	C_{A1}	C_{A2}	C_{A3}

- 3 ways to determine ($-dC_A/dt$) from concentration - time data 1

2A. Graphical





2. Differential Method III

- 3 ways to determine ($-dC_A/dt$) from concentration
  - time data 2

2B. Polynomial (using Polymath)

$C_A = a_o + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$

$$\frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + 4a_4 t^3$$

2C. Finite Difference (5 pts)

$$\left.\frac{dC}{dt}\right)_0 = \frac{-3C_0 + 4C_1 - C_2}{2\Delta t} \qquad \left.\frac{dC}{dt}\right)_i = \frac{C_{i+1} - C_{i-1}}{2\Delta t}$$

- last point $$\left.\frac{dC}{dt}\right)_5 = \frac{C_3 - 4C_4 + 3C_5}{2\Delta t}$$

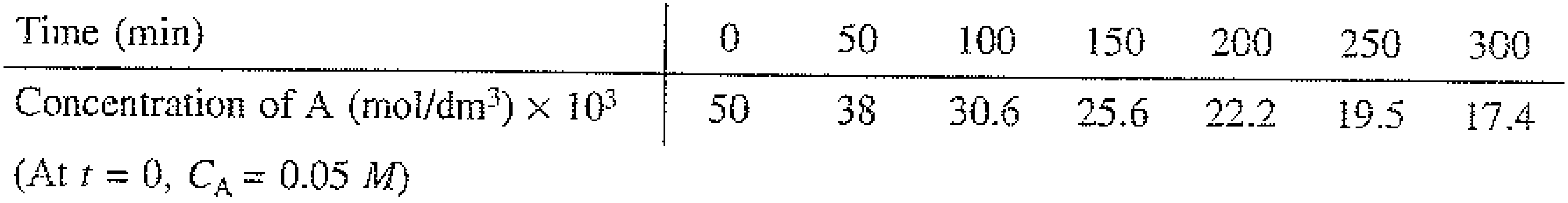
2. Differential Method IV

- **Ex 5-2, p 260 Determining the rate law 1**

  Trytil (A) + Methanol (B) → Products

  - Reaction carried out at benzene and pyridine solution at 25°C (at t = 0, C_A = 0.05 M , C_B = 0.5 M)

  - One product Cl reacts with pyridine and precipitates



Time (min)	0	50	100	150	200	250	300
Concentration of A (mol/dm^3) × 10^3	50	38	30.6	25.6	22.2	19.5	17.4

(At $t = 0$, $C_A = 0.05$ M)

2. Differential Method V

○ **Ex 5-2, Determining the rate law 2**

- Determine the rxn order wrt trytil

- If rxn order wrt methanol was 1st, k = ?

Sol)

- Postulate a rate law $-r_A = kC_A^{\alpha}C_B^{\beta}$

- Process data in terms of measurable variable ⇒ C_A

- Look for simplifications

- **$C_B >> C_A$ (10 times) ⇒ $C_B = C_{B0}$**
- **substituting,**

$$-r_A = \underbrace{kC_{B0}^{\beta}}_{k'}C_A^{\alpha} = k'C_A^{\alpha}$$

2. Differential Method VI

- Ex 5-2, Determining the rate law 3

  - Applying CRE algorithm

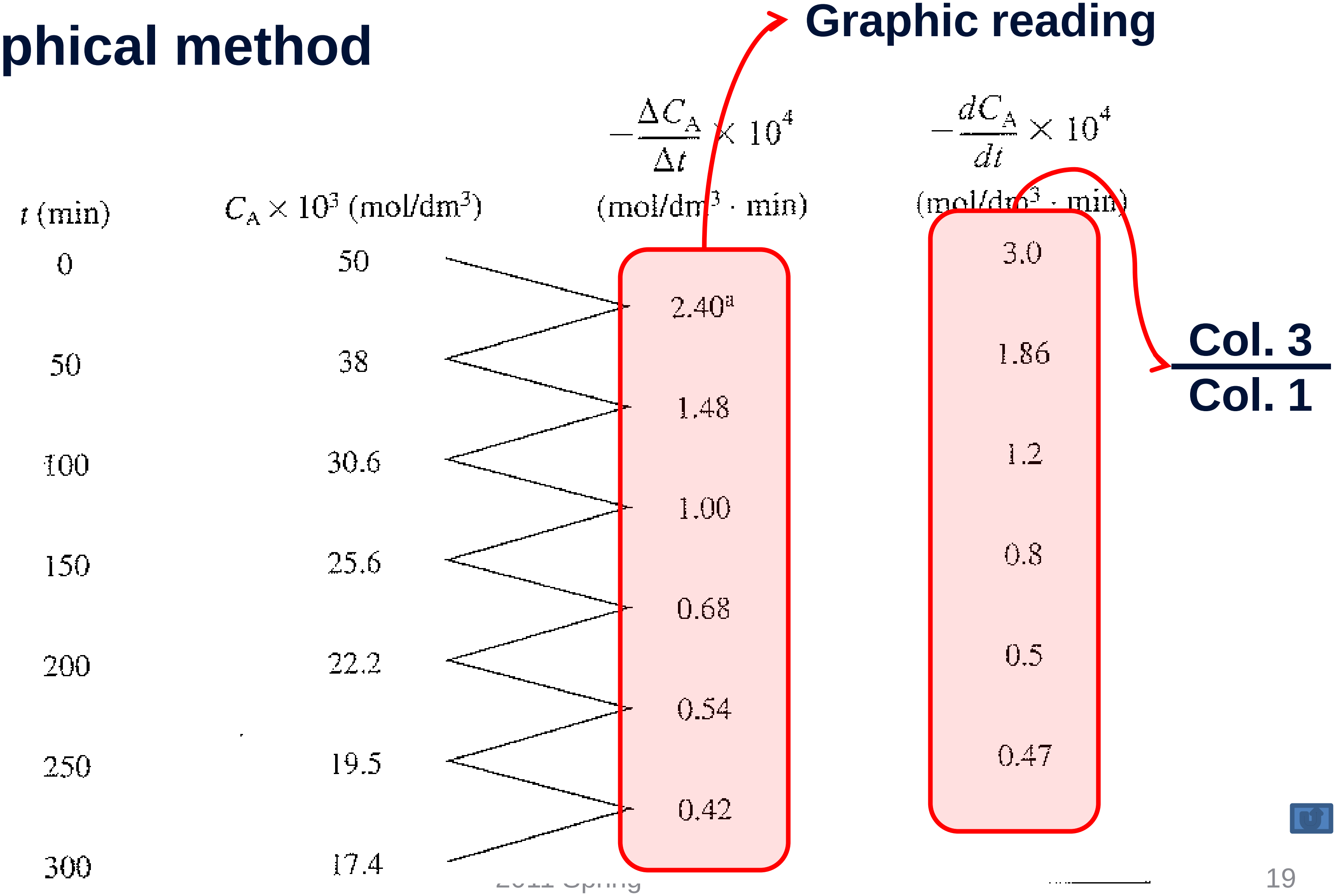
    - mole balance $$\frac{dN_A}{dt} = r_A V$$
    - rate law

$$-r_A = k' C_A^{\alpha}$$

  - stoichiometry: liquid, $V = V_0$ $$C_A = \frac{N_A}{V_0}$$
  - combine $$-\frac{dC_A}{dt} = k C_A^{\alpha}$$
  - taking natural log $$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

2. Differential Method VII

- Ex 5-2, Determining the rate law 4
  - Graphical method



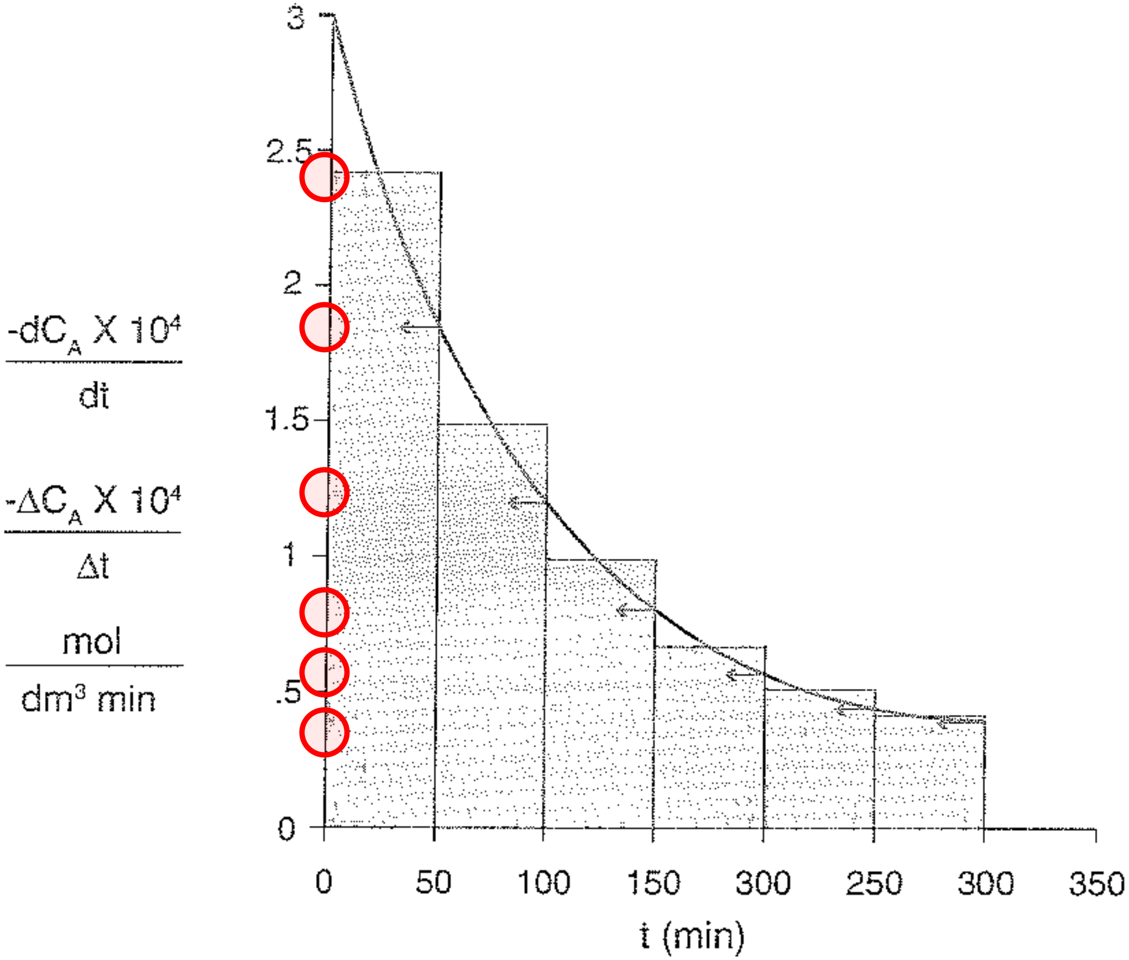
Graphic reading

t (min)	$C_A \times 10^3$ (mol/dm^3)	$-\frac{\Delta C_A}{\Delta t} \times 10^4$ (mol/dm^3 · min)	$-\frac{dC_A}{dt} \times 10^4$ (mol/dm^3 · min)
0	50		3.0
		2.40[a]	
50	38		1.86
		1.48	
100	30.6		1.2
		1.00	
150	25.6		0.8
		0.68	
200	22.2		0.5
		0.54	
250	19.5		0.47
		0.42	
300	17.4		

$$\frac{\text{Col. 3}}{\text{Col. 1}}$$

2. Differential Method VIII

- **Ex 5-2, Determining the rate law 5**



2. Differential Method IX

- ○ **Ex 5-2, Determining the rate law 6**

  - Finite difference method 1

$$t = 0 \qquad \left(\frac{dC_A}{dt}\right)_{t=0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

$$= \frac{[-3(50) + 4(38) - 30.6] \times 10^{-3}}{100}$$

$$= -2.86 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

$$-\frac{dC_A}{dt} \times 10^4 = 2.86\ \text{mol/dm}^3 \cdot \text{min}$$

$$t = 50 \qquad \left(\frac{dC_A}{dt}\right)_1 = \frac{C_{A2} - C_{A0}}{2\Delta t} = \frac{(30.6 - 50) \times 10^{-3}}{100}$$

$$= -1.94 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

2. Differential Method X

- **Ex 5-2, Determining the rate law 7**

  - Finite difference method 2

$$t = 100 \quad \left(\frac{dC_A}{dt}\right)_2 = \frac{C_{A3} - C_{A1}}{2\Delta t} = \frac{(25.6 - 38) \times 10^{-3}}{100}$$

$$= -1.24 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

$$t = 150 \quad \left(\frac{dC_A}{dt}\right)_3 = \frac{C_{A4} - C_{A2}}{2\Delta t} = \frac{(22.2 - 30.6) \times 10^{-3}}{100}$$

$$= -0.84 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

$$t = 200 \quad \left(\frac{dC_A}{dt}\right)_4 = \frac{C_{A5} - C_{A3}}{2\Delta t} = \frac{(19.5 - 25.6) \times 10^{-3}}{100}$$

$$= -0.61 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

$$t = 250 \quad \left(\frac{dC_A}{dt}\right)_5 = \frac{C_{A6} - C_{A4}}{2\Delta t} = \frac{(17.4 - 22.2) \times 10^{-3}}{100}$$

$$= -0.48 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

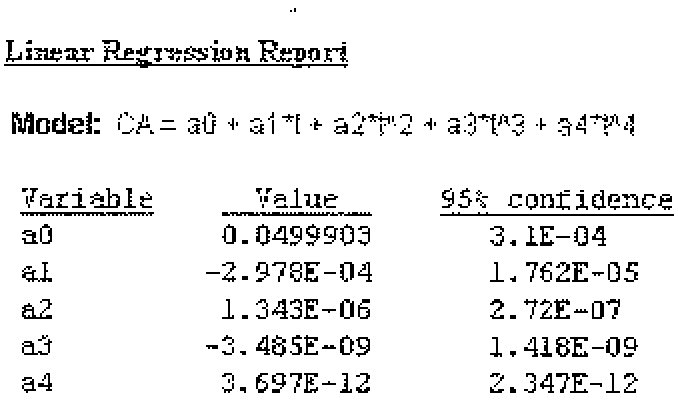
$$t = 300 \quad \left(\frac{dC_A}{dt}\right)_6 = \frac{C_{A4} - 4C_{A5} + 3C_{A6}}{2\Delta t} = \frac{[22.2 - 4(19.5) + 3(17.4)] \times 10^{-3}}{100}$$

$$= -0.36 \times 10^{-4}\ \text{mol/dm}^3 \cdot \text{min}$$

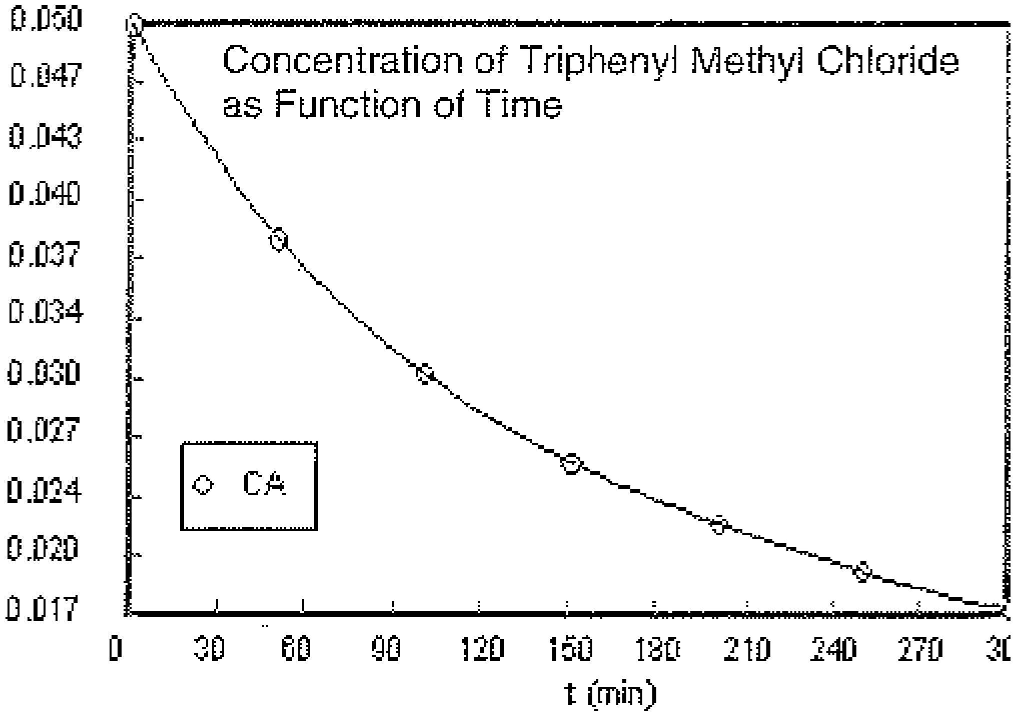
2. Differential Method XI

- Ex 5-2, Determining the rate law 8

  - Polynomial method



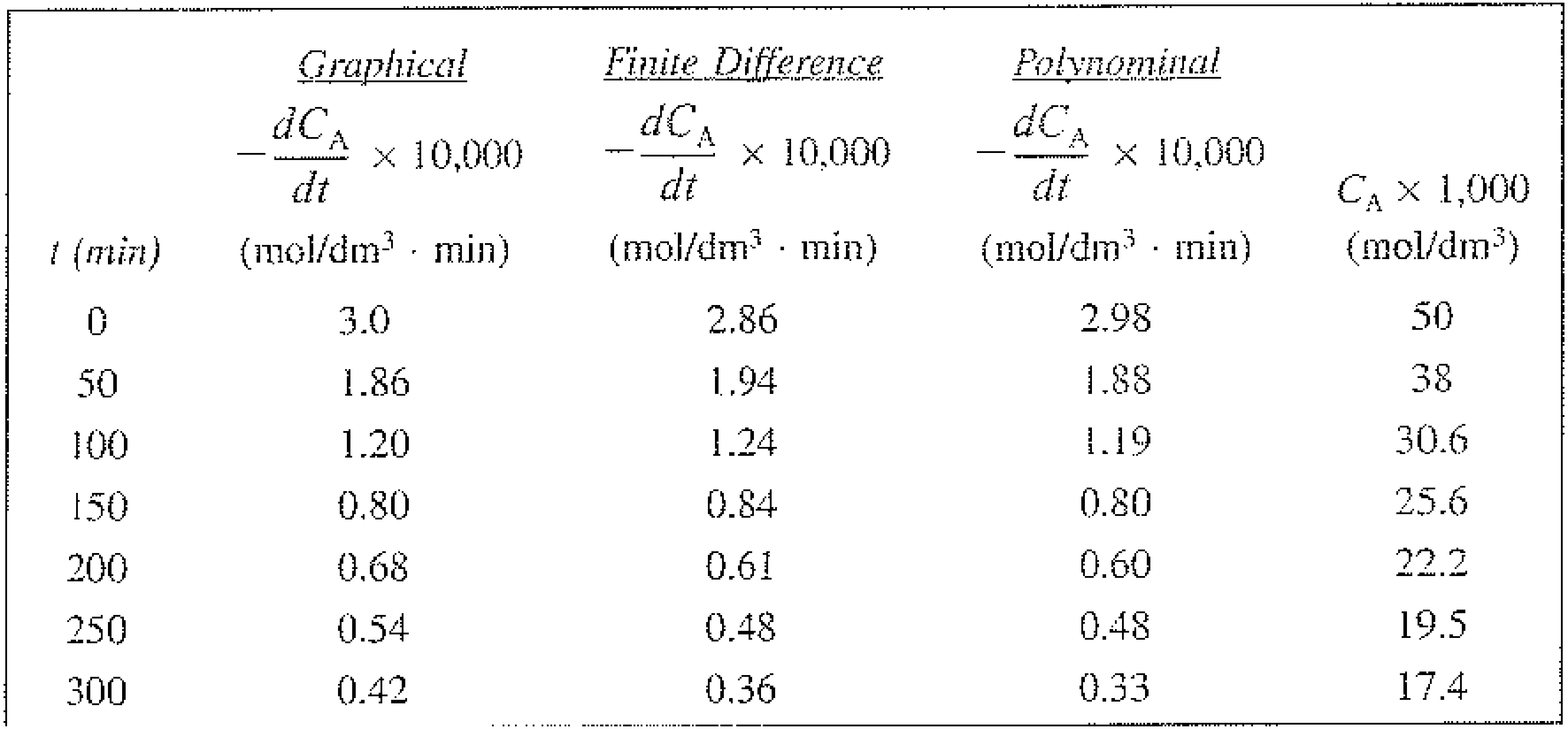
```
Linear Regression Report

Model: CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4

Variable          Value        95% confidence
a0             0.0499903          3.1E-04
a1            -2.978E-04          1.762E-05
a2             1.343E-06          2.72E-07
a3            -3.485E-09          1.418E-09
a4             3.697E-12          2.347E-12
```



2. Differential Method XII

- **Ex 5-2, Determining the rate law 9**

  - Comparison



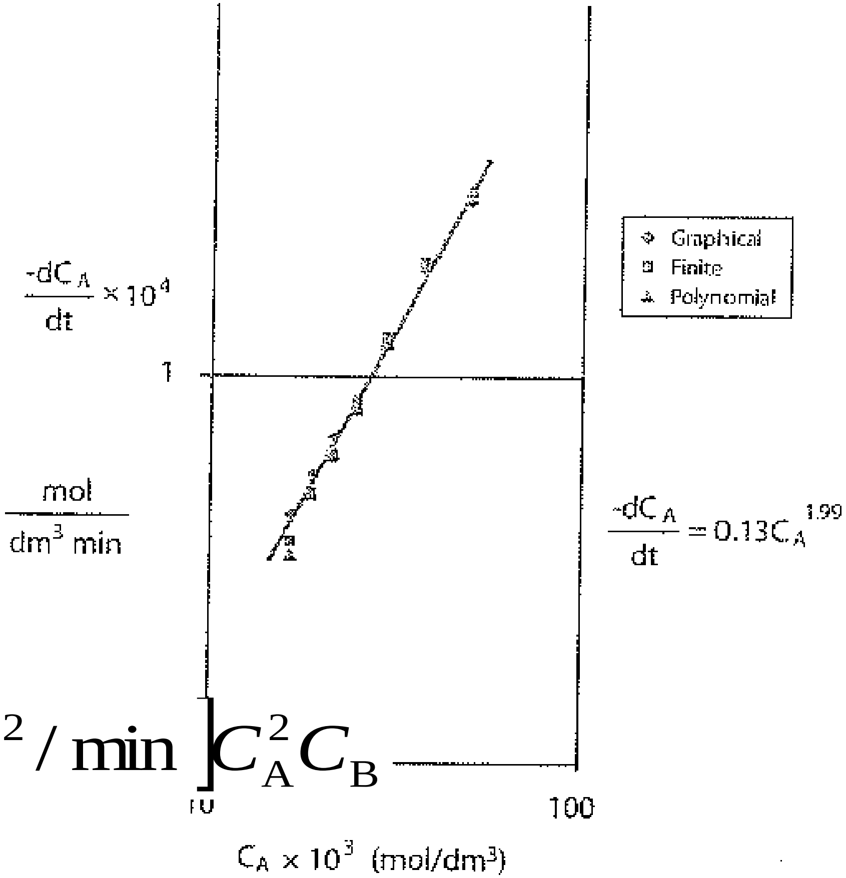
	Graphical	*Finite Difference*	*Polynominal*	
t (min)	$-\frac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	$-\frac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	$-\frac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	$C_A \times 1{,}000$ (mol/dm^3)
0	3.0	2.86	2.98	50
50	1.86	1.94	1.88	38
100	1.20	1.24	1.19	30.6
150	0.80	0.84	0.80	25.6
200	0.68	0.61	0.60	22.2
250	0.54	0.48	0.48	19.5
300	0.42	0.36	0.33	17.4

2. Differential Method XIII

○ **Ex 5-2, Determining the rate law 10**

- Plot column 2,3, and 4 as a function of column 5

- **k' = 0.125(graph),**
  0.122(regression)
  0.13(excel,
  with α = 1.99)
- **with α = 2.0**
  k' = 0.122



- Rate law

$$-r_A = \left[0.244\,(\text{dm}^3/\text{mol})^2/\text{min}\right] C_A^2 C_B$$

3. Non-Linear Least-Squares Analysis I

- Given concentration as a function of time from batch reactor experiments

time (s)	0	t_1	t_2	t_3
concentration (mol/dm^3)	C_{Ao}	C_{A1}	C_{A2}	C_{A3}

- Find the parameter values (α, k, E) for which the sum of the squares of the differences, the measured parameter (P_m), and the calculated parameter (P_c) is a minimum

$$\sigma^2 = \sum_{i=1}^{n} \frac{\left(P_{mi} - P_{ci}\right)^2}{N - K}$$

3. Non-Linear Least-Squares Analysis II

○ **For concentration-time data**

- **Measured parameter P has concentration C_A**
  - **integrate the combined mole balance equation and rate law**

$$\frac{dC_A}{dt} = -kC_A^{\alpha}$$

- **Integrate**

$$C_A = \left[C_{A0}^{1-\alpha} - (1-\alpha)kt\right]^{\frac{1}{1-\alpha}}$$

- **Guess α and k and calculate each C_{ACi} at the times shown in the above table**
- **Then compare it with the measured concentration by taking the difference and squaring it.**

3. Non-Linear Least-Squares Analysis III

- ○ **Then sum up the differences for all the data points**

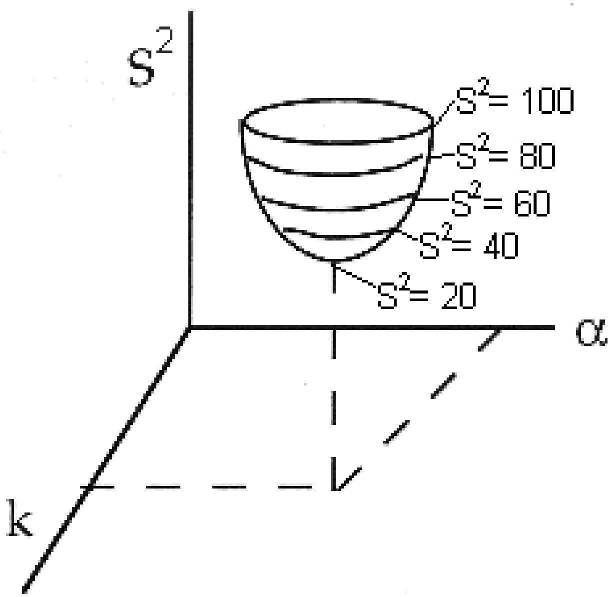
$$s^2 = \sum_{i=1}^{N} \left(C_{Ami} - C_{Aci}\right)^2 = \sum_{i=1}^{N} \left(C_{Ami} - \left[C_{Ao}^{1-\alpha} - (1-\alpha)kt_i \right]^{1/1-\alpha} \right)^2$$

- ○ **Continue to guess *k* and *α* until we find the values of alpha and *k* which minimize S^2**

  (actually we let the computer

  find these values)

  - Ex 5-3, p 274 Solve!!



4. Initial Rate Method

○ **Presence of significant reverse rxn**

- Even the differential method is ineffective

- A series of experiment at different initial conc.

- **C_{A0} with $-r_{A0}$ determined for each run**
- **differentiating the data and extrapolating to 0 point**

- If the rate law is

$$-r_{A0} = kC_{A0}^{\alpha}$$

- **the plot $\ln(-r_{A0})$ vs. $\ln C_{A0}$ ⇒ rxn order α by slope**

$$\boxed{\ln(-r_{A0}) = \ln k + \alpha \ln C_{A0}}$$

Ex 5-4, p 278, Solve!!!

5. Half-Lives Method I

- **Time it takes for the conc. of the reactant to fall to half of its initial value**
  - **Start with irreversible rxn, A → Products**

$$-r_{\mathrm{A}} = kC_{\mathrm{A}}^{\alpha}$$

  - **Rate law**

$$-\frac{dC_{\mathrm{A}}}{dt} = -r_{\mathrm{A}} = kC_{\mathrm{A}}^{\alpha}$$

  - **Integrating with $C_{\mathrm{A}} = C_{\mathrm{A0}}$ at $t = 0$**

$$t = \frac{1}{k(\alpha-1)}\left(\frac{1}{C_{\mathrm{A}}^{\alpha\text{-}1}} - \frac{1}{C_{\mathrm{A0}}^{\alpha\text{-}1}}\right)$$

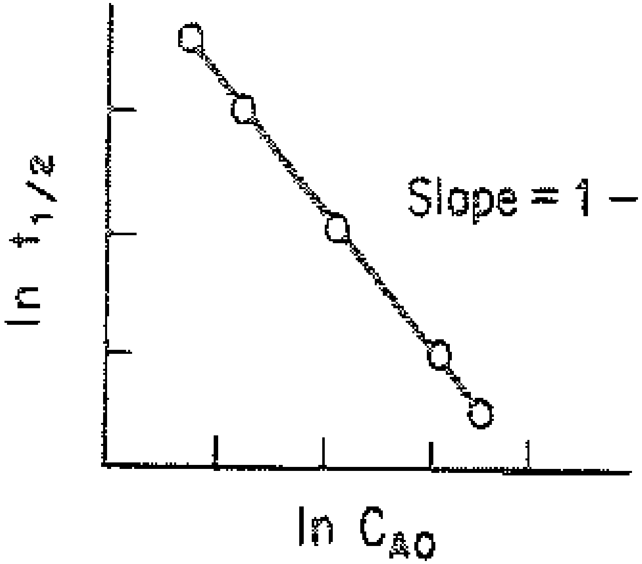
$$= \frac{1}{kC_{\mathrm{A0}}^{\alpha\text{-}1}(\alpha-1)}\left[\left(\frac{C_{\mathrm{A0}}}{C_{\mathrm{A}}}\right)^{\alpha-1} - 1\right]$$

5. Half-Lives Method II

- **Half life = time required for the conc. to drop to half of its initial value**

  - $$t = t_{1/2} \quad \text{when}\ C_A = \frac{1}{2} C_{A0}$$

$$t_{1/2} = \frac{2^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{A0}^{\alpha\text{-}1}}\right)$$



  - **Taking natural log**

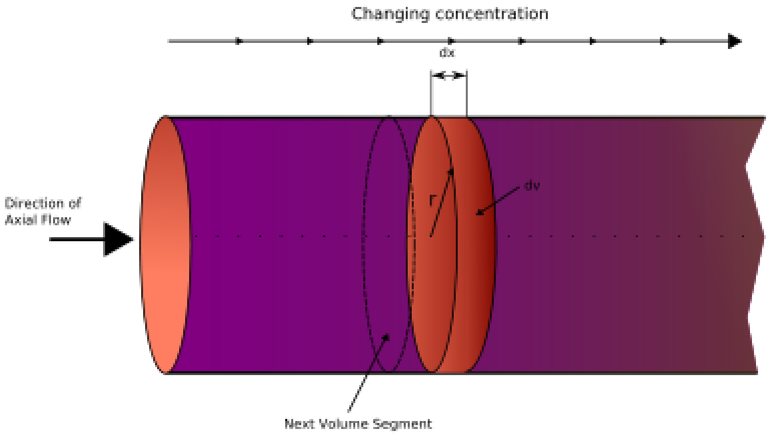
$$\ln t_{1/2} = \ln \frac{2^{\alpha-1}-1}{(\alpha-1)k} + (1-\alpha)\ln C_{A0}$$

6. Differential Reactors I

○ **Structure**

- A tube containing a very small amount of catalyst

- usually in the form of thin wafer of disk
- conversion of the reactant in the bed is extremely small ⇒ $C_A \approx C_{A0}$
- the reactor is considered to be gradientless or spatially uniform
- easy to construct
- heat negligible



6. Differential Reactors II

- **Design equation 1**

$$\begin{bmatrix}\text{Flow}\\ \text{rate in}\end{bmatrix}-\begin{bmatrix}\text{Flow}\\ \text{rate out}\end{bmatrix}+\begin{bmatrix}\text{Rate of}\\ \text{gen.}\end{bmatrix}=\begin{bmatrix}\text{Rate of}\\ \text{accum.}\end{bmatrix}$$

$$[F_{\mathrm{A0}}] - [F_{\mathrm{A}e}] + \left[\left(\frac{\text{Rate of rxn}}{\text{Mass of cat}}\right)(\text{Mass of cat})\right] = 0$$

$$F_{\mathrm{A0}} - F_{\mathrm{A}e} + \left(-r_A^{'}\right)\left(\Delta W\right) = 0$$

- Solving for –*r*’$_A$

$$-r_A^{'} = \frac{F_{\mathrm{A0}} - F_{\mathrm{A}e}}{\Delta W}$$

6. Differential Reactors III

○ **Design equation 2**

- In terms of concentration

$$\boxed{-r_A^{'} = \frac{v_0 C_{\mathrm{A0}} - v C_{\mathrm{A}e}}{\Delta W}}$$

- In terms of conversion or product flow rate F_{p}

$$\boxed{-r_A^{'} = \frac{F_{\mathrm{A0}} X}{\Delta W} = \frac{F_{\mathrm{P}}}{\Delta W}}$$

- Constant volumetric flow rate

$$-r_A^{'} = \frac{v_0 (C_{\mathrm{A0}} - C_{\mathrm{A}e})}{\Delta W} = \frac{v_0 C_{\mathrm{P}}}{\Delta W}$$

- Since $C_A \approx C_{A0}$, $-r'_A = -r'_A(C_A)$

R5.4 Laboratory Reactors I

- **The successful design of industrial reactors**
  - **Reliability of the experimentally determined parameters used in the scale-up**
  - **It is imperative to design equipment and experiments that will generate accurate and meaningful data.**
  - **Usually, no single comprehensive laboratory reactor that could be used for all types of reactions and catalysts[closely follow the excellent strategy presented in the article by V. W. Weekman of Mobil Oil]**

R5.4 Laboratory Reactors II

- **Criteria used to evaluate various types of laboratory reactors**

CRITERIA USED TO EVALUATE LABORATORY REACTORS
1. Ease of sampling and product analysis
2. Degree of isothermality
3. Effectiveness of contact between catalyst and reactant
4. Handling of catalyst decay
5. Reactor cost and ease of construction

R5.4 Laboratory Reactors III

○ **Integral (Fixed-Bed) Reactor 1**

- Advantages

- **ease of construction**
- **the channeling or bypassing of some of the catalyst by the reactant stream may not be as fatal to data interpretation in the case of this reactor as in that of the differential reactor**
- **more product will be formed ⇒ the problems encountered in the differential reactor in analyzing small or trace amounts of product in the effluent stream are eliminated**

R5.4 Laboratory Reactors IV

○ **Integral (Fixed-Bed) Reactor 2**

- Disadvantages 1

- more product will be formed ⇒ if a reaction is highly endothermic or exothermic, significant axial and radial temperature gradients can result, and this reactor will receive a poor-to-fair rating on its degree of isothermality
- if a reaction follows different reaction paths with different activation energies, different products will be formed at different temperatures

  ⇒ difficult to unscramble the data to evaluate the various reaction rate constants because the reaction mechanism changes with changing temperature along the length of the reactor

R5.4 Laboratory Reactors V

○ **Integral (Fixed-Bed) Reactor 3**

- Disadvantages 2
  - if the catalyst decays significantly during the time an experiment is carried out, the reaction rates will be significantly different at the end of the experiment than at the start of the experiment
  - the reaction may follow different reaction paths as the catalyst decays, so that the selectivity to a particular product will vary during the course of the experiment

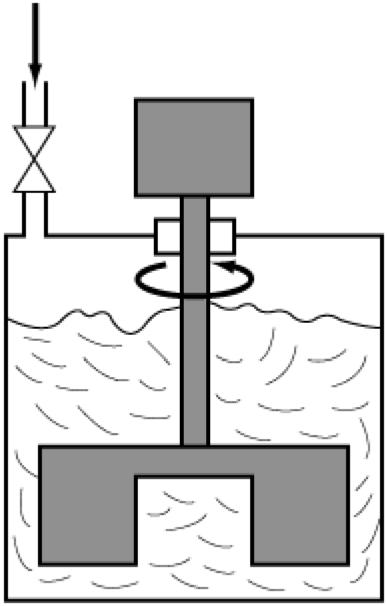
  ⇒ it will be difficult to sort out the various rate law parameters for the different reactions and, as a result, this reactor receives a poor rating in the catalyst decay category

☞Relatively easy and inexpensive to construct, so it receives a high rating in the construction category.

R5.4 Laboratory Reactors VI

○ **Stirred-Batch Reactor 1**

- Catalyst is dispersed as a slurry
- Better contact between the catalyst and fluid than either the differential or integral reactors
- A sampling problem ⇒ stopping the reaction 1
  - samples of fluid are usually passed through cyclones or withdrawn through filters or screens to separate the catalyst and fluid

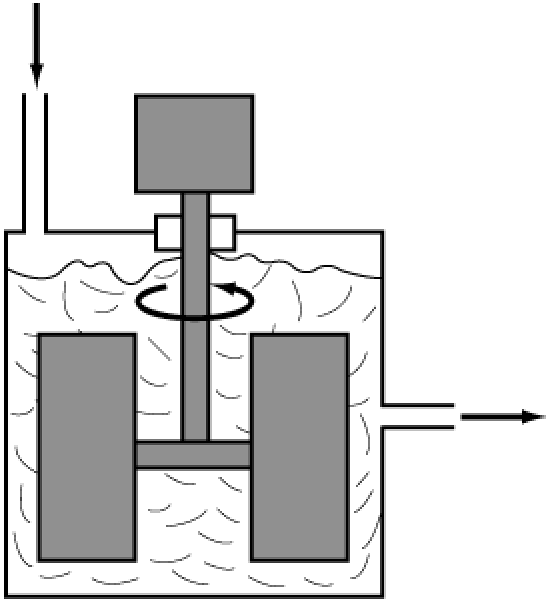


R5.4 Laboratory Reactors VII

- **Stirred-Batch Reactor 2**
  - **A sampling problem ⇒ stopping the reaction 2**
    - **slow quenching of the reaction in the cyclone or plugging of the filter sampling system by the catalyst particles is a constant concern, thus making the rating in the sampling category only fair.**
  - **Well mixed, its isothermality is good**
  - **Good contact between the catalysts and reactants,**
  - **contact time is known since the catalyst and reactants are fed at the same time**
  - **If the catalyst decays, the activity and selectivity will vary during the course of data collection**

R5.4 Laboratory Reactors VIII

- Stirred Contained-Solids Reactor (SCSR) 1
  - Catalyst particles are contained in paddles that rotate at sufficiently high speeds to minimize external mass transfer effects
  - Keep the fluid contents well mixed
    - isothermal conditions can be maintained
    - good contact between the catalyst and fluid



R5.4 Laboratory Reactors IX

- ○ **Stirred Contained-Solids Reactor (SCSR) 2**

- If the catalyst particle size is small, difficulties could be encountered containing the particles in the paddle screens

⇒It receives only a fair rating in the ease of construction and cost category.

☞ Good rating for ease of sampling and analysis of product composition

☞ Suffers from being unable to generate useful data when the catalyst being studied decays

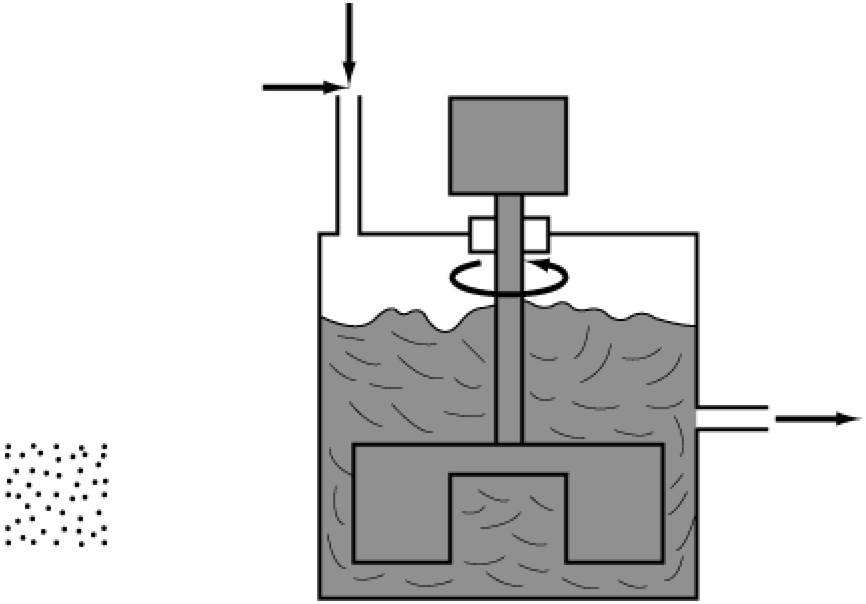
R5.4 Laboratory Reactors X

○ **Continuous-Stirred Tank Reactor (CSTR) 1**

- Fresh catalyst is fed to the reactor along with the fluid feed
- The catalyst leaves the reactor in the product stream at the same rate that it is fed

⇒ the catalyst in the reactor is at the same level of catalytic activity at all times

☞ Not faced with the problem encountered in the four previous reactors



R5.4 Laboratory Reactors XI

○ **Continuous-Stirred Tank Reactor (CSTR) 2**

- **Distribution of time that the catalyst particles have been in the reactor, there will be a distribution of catalytic activities of the particles in the bed**

  ⇒ The mean activity of a catalyst decay

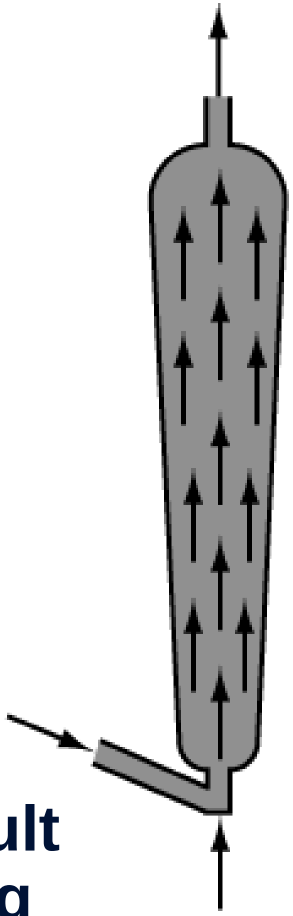
  - **if the mean residence time is large, selectivity disguise could be a problem**

- **Reactor is well-mixed, isothermality and fluid--solid contact categories are rated as good**
- **Difficulties can arise in feeding the slurry accurately**
  - **it is difficult to quench the reaction product**

☞ **Only fair ratings in the first (sampling) and fifth (construction) categories.**

R5.4 Laboratory Reactors XII

- Straight-Through Transport Reactor 1
  - Commercially used widely in the production of gasoline from heavier petroleum fractions
  - Used in grain drying operations
  - Either an inert gas or the reactant itself transports the catalyst through the reactor
    - any possibility of catalyst decay/selectivity disguise is virtually eliminated because the catalyst and reactants are fed continuously
  - For highly endothermic or exothermic reactions, isothermal operation will be difficult to achieve and it receives a poor-to-fair rating in this category



R5.4 Laboratory Reactors XIII

- Straight-Through Transport Reactor 2
  - At moderate or low gas velocities there may be slip between the catalyst particles and the gas so that the gas-catalyst contact time will not be known very accurately ⇒ Fair-to-good rating in the gas-catalyst contacting category
  - Somewhat easier to construct than the CSTR, but salt or sand baths may be required to try to maintain isothermal operation

  ⇒ Fair-to-good rating in the construction category
  - Difficulty in separating the catalyst and reactant gas or in thermally quenching the reaction

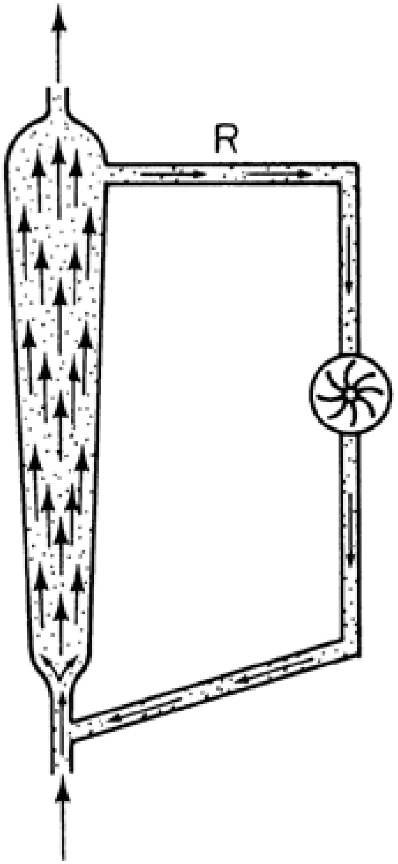
  ⇒ Fair rating in the sampling category.

R5.4 Laboratory Reactors XIV

- **Recirculating Transport Reactor 1**

  - By recirculating the gas and catalyst through the transport reactor, a well-mixed condition can be achieved provided that the recirculation rate is large with respect to the feed rate

  ⇒ isothermal operation is achieved



R5.4 Laboratory Reactors XIV

- **Recirculating Transport Reactor 2**
  - **Operated at steady state**
    - **the kinetic parameters measured at the start of the experiment will be the same as those measured at the end**
  - **Fresh catalyst is mixed with decayed catalyst from the recycle, the product distribution and the kinetic parameters might not be the same as those measured in a straight-through transport reactor where the gas "sees" only fresh catalyst.**
  - **The incorporation of a recirculation system adds a degree of complexity to the construction, which gives it a lower rating in this category as well.**